

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 220/04, 220/34, 8/00, 212/14, 220/60, 230/02, C09D 157/00	A1	(11) International Publication Number: WO 97/31042 (43) International Publication Date: 28 August 1997 (28.08.97)
(21) International Application Number: PCT/US97/00726 (22) International Filing Date: 14 January 1997 (14.01.97) (30) Priority Data: 08/606,179 23 February 1996 (23.02.96) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). (72) Inventors: SCHMIDT, Donald, L.; 2412 St. Marys Drive, Midland, MI 48640 (US). ROSE, Gene, D.; 216 East St. Andrews Road, Midland, MI 48642 (US). MILLER, Barbara, A.; 3001 Jeffrey Lane, Midland, MI 48640 (US). (74) Agent: WILLIS, Reid, S.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, BR, CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: REVERSIBLE AND IRREVERSIBLE WATER-BASED COATINGS (57) Abstract A composition comprising an aqueous-based solvent and a water-soluble or water-dispersible polymer that is characterized by having a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion is described. A water-resistant, fast dry-to-the-touch coating that does not release noxious gases can be prepared by applying the composition to a substrate. The coating can be designed to be either permanent, or removable by the addition of mild acids such as aqueous solutions of vinegar or citric acid.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

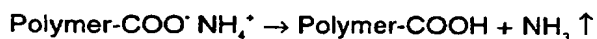
REVERSIBLE AND IRREVERSIBLE WATER-BASED COATINGS

The invention relates to water-dispersible polymeric compositions that can be used to prepare removable or permanent coatings.

Coatings are generally made to provide a protective barrier for applications such as floors, automobiles, exteriors and interiors of houses, and human skin. Protective coatings for floors, for example, have been known since the mid 1950s. Many of the early coating materials were applied using petroleum- or naphthene-based solvents and as such were undesirable due to the toxicity and flammability of these solvents.

Water-based synthetic emulsion compositions such as styrene resin emulsions, styrene-acrylate copolymer resin emulsions, and acrylate emulsions, developed in the early 1960s, gradually replaced organic solvent-based compositions. Although the water-based compositions are preferable to organic solvent-based compositions, they suffer from the disadvantage of being difficult to remove in an application where removability is desired. Removal of coating may be desirable because even the most durable coatings tend to deteriorate due to soiling or wear and tear. In other applications, such as protective care products for the skin, the advantages of water-based removable coatings are obvious.

Removable, water-based coatings are known. For example, polymers that contain ammonium carboxylate functionality are water compatible, but become incompatible through the loss of solvent and ammonia.



water-compatible

water-incompatible

Water-resistant coatings made by the above-illustrated process can be subsequently removed by contact with an aqueous alkaline liquid, which converts the acid back into the compatible salt.

The ammonium carboxylate coating suffers from several disadvantages:
1) the formulations are malodorous and irritating to the eyes and skin; 2) long set

times are required to attain acceptable physical properties of the coating; and 3) the removal or stripping process requires the use of hazardous alkaline liquids.

For example, in U.S. Patent 4,622,360, Gomi et al. discloses a removable water-borne polyurethane resin containing carboxyl groups. Coating compositions
5 can be prepared by adding a polyvalent complex-forming metal to the water-borne resin. The polyvalent metal forms a stable water-dispersible complex with the resin in the aqueous solution. When the dispersion is applied to a floor surface, noxious volatile materials evaporate to allow the polyvalent metal ions to initiate a crosslinking
10 of two or more carboxyl groups, thereby forming a hardened, water-incompatible coating. This hardened coating can be removed, but only with a harsh alkaline solution containing ligands such as ethylene diamine tetraacetic acid.

In view of the deficiencies of the known art, it would be desirable to have a composition that provides a coating that rapidly dries to the touch at ambient temperatures and that can be designed to be either permanent or easily removed
15 without the use of harsh solvents.

It would further be useful to have a hypoallergenic, non-toxic, water-based composition that provides a coating that gives long-lasting protection to the skin against sun, dryness, and harsh chemicals, but that can be easily removed without the use of harsh chemicals.

20 The present invention is an organic polymer comprising a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion.

In a second aspect, the present invention is a method of preparing a composition comprising an aqueous-based solvent and a water-compatible polymer
25 that is soluble in the water-based solvent, the polymer having a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion, the method which comprises the steps of:

a) preparing a solution comprising a first aqueous-based solvent and a polymer having a backbone that contains at least one pendant weak

acid group and at least one pendant strong cationic group associated with a non-bicarbonate counterion;

b) adding sufficient base to the solution to precipitate at least a portion of the polymer;

5 c) washing the precipitate with water; and

d) contacting the precipitate with a second aqueous-based solvent and a sufficient amount of carbon dioxide or carbonic acid to render the precipitate soluble in the second aqueous-based solvent.

10 In a third aspect, the present invention is a method of preparing a stable aqueous dispersion of a polymer having a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion, the method which comprises the steps of:

15 a) preparing a stable aqueous dispersion of a polymer having weak acid groups, and strong cationic groups associated with non-bicarbonate counterions; and

b) exchanging at least a portion of the non-bicarbonate counterions with bicarbonate counterions.

20 A water-resistant, fast dry-to-the-touch, non-tacky coating that can be formed at room temperature and does not release noxious volatile materials is inherently prepared from the composition of the present invention. This coating can be designed to be either permanent, or removable by contact with even mildly acidified aqueous-based solvents such as aqueous solutions containing vinegar or citric acid.

25 The polymer of the present invention, which is preferably a water-compatible polymer, is characterized by having a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion. As used herein, the term "water-compatible polymer" refers to a polymer which will form a stable or metastable mixture with water, including a solution, a colloidal suspension, a stable emulsion or a dispersion. The term "strong cationic group" refers to a cation having a charge that is independent of pH. The term "weak

acid group" refers to an acid having a pK_a in the range of from 2 to 7. Similarly, the term "anion of a weak acid group" refers to an anion of an acid having a pK_a from 2 to 7. Preferably, the polymer backbone contains a plurality of weak acid pendant groups, anions of weak acid pendant groups, and strong cation pendant groups.

- 5 Preferably, the mole-to-mole ratio of weak pendant acid groups plus anions of weak acid groups to strong cationic pendant groups is not less than 0.3, more preferably not less than 0.5, most preferably not less than 0.7. Preferably, the ratio of weak pendant acid groups plus anions of weak acid groups to strong cation pendant groups is not more than 3.3, more preferably not more than 2, and most preferably
- 10 not more than 1.4.

- A polymer having a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion can be prepared by the polymerization of a bicarbonate salt of a polymerizable strong cationic monomer and a polymerizable weak acid monomer optionally in the
- 15 presence of a carbon dioxide cosolvent. The polymer can also be prepared by first preparing a polymer precursor containing a weak acid group and a strong cationic group associated with a non-bicarbonate counterion such as a halide, a nitrate, a sulfate, or a salt of a sulfonic acid ($R-SO_3^-$), more preferably a halide, most preferably chloride.

- 20 The polymer precursor can be prepared in a variety of ways including:
- a) copolymerization of a polymerizable monomer having a weak acid group and polymerizable monomer having a strong cationic group associated with a non-bicarbonate counterion; b) polymerization of a polymerizable monomer that contains both weak acid and strong cationic functionality; or c) post reaction of a polymer
- 25 having reactive functionality. The polymer preparation preferably includes a non-interfering, polymerizable monomer (units of which are represented by D in the structural depiction of the polymer). The term "non-interfering, polymerizable monomer" is used herein to refer to one or more monomers that do not adversely affect the formation and properties of a coating prepared from the polymer.

- 30 Suitable polymerizable monomers containing a weak acid group include ethylenically unsaturated compounds having carboxylic acid, phenolic, thiophenolic, and phosphinyl functionality. Examples of suitable polymerizable monomers include

acrylic acid, methacrylic acid, itaconic acid, β -carboxyethyl acrylate (usually as a mixture of acrylic acid oligomers), vinylbenzoic acid, vinylchlorophenol, vinylbromophenol, vinylthiophenol, and 2-propenoic acid: 2-methyl-, (hydroxyphosphinyl) methyl ester.

- 5 Suitable polymerizable monomers containing a strong cation group associated with a non-bicarbonate counterion include salts of ethylenically unsaturated compounds having quaternary ammonium, sulfonium, cyclic sulfonium, and phosphonium functionality. Examples of suitable monomers having quaternary ammonium functionality include ethylenically unsaturated trialkylammonium salts
 10 such as vinylbenzyl tri- C_1 - C_4 -alkylammonium chloride or bromide; trialkylammoniumalkyl acrylates or methacrylates such as 2-[(methacryloyloxy)ethyl]-trimethylammonium chloride and N, N-diethyl-N-methyl-2-[(1-oxo-2-propenyl)oxy]ethanaminium methyl sulfate (Chem. Abstracts Reg. No. 45076-54-8); and trialkylammoniumalkyl acrylamides such as N,N,N-trimethyl-3-[(2-methyl-1-oxo-2-
 15 propenyl) amino]-1-propanaminium chloride (Chem. Abstracts Reg. No. 51441-64-6) and N, N-dimethyl-N-[3-[(2-methyl-1-oxo-2-propenyl)amino]propyl]-benzenemethaminium chloride (Chem. Abstracts Reg. No. 122988-32-3).

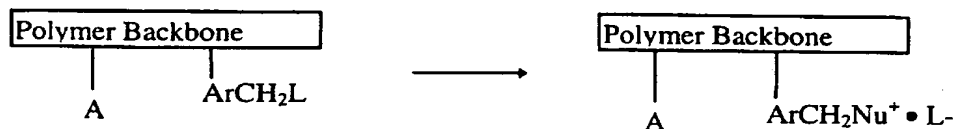
- Examples of polymerizable unsaturated sulfonium salts include dialkylsulfonium salts such as [4-ethoxy-3-(ethoxycarbonyl)-2-methylene-4-
 20 oxobutyl]dimethylsulfonium bromide (Chem. Abstracts Reg. No. 63810-34-4); and vinylbenzyl dialkylsulfonium salts such as vinylbenzyl dimethylsulfonium chloride. Examples of polymerizable cyclic sulfonium salts include 1-[4-[(ethenylphenyl)-methoxy]phenyl]tetrahydro-2H-thiopyranium chloride (Chem. Abstracts Reg.
 No. 93926-67-1); and vinylbenzyl tetrahydrothiophenonium chloride, which can be
 25 prepared by the reaction of vinylbenzyl chloride with tetrahydrothiophene.

- Examples of polymerizable phosphonium salts include 2-methacryloxyethyltri- C_1 - C_{20} -alkyl-, aralkyl-, or aryl-phosphonium salts such as 2-methacryloxyethyltri-n-octadecylphosphonium halide (Chem. Abstracts Reg. No. 166740-88-1); tri- C_1 - C_{18} -alkyl-, aralkyl-, or aryl-vinylbenzyl-phosphonium salts such as trioctyl-3-vinylbenzyl-
 30 phosphonium chloride, trioctyl-4-vinyl-benzylphosphonium chloride (Chem. Abstracts Reg. No. 15138-12-4), tributyl-3-vinylbenzylphosphonium chloride, tributyl-4-vinylbenzylphosphonium chloride (Chem. Abstracts Reg. No. 149186-03-8), triphenyl-

- 3-vinylbenzylphosphonium chloride, and triphenyl-4-vinylbenzylphosphonium chloride (Chem. Abstracts Reg. No. 145425-78-1); C_3 - C_{18} -alkenyltrialkyl-, aralkyl-, or aryl-phosphonium salts such as 7-octenyltriphenylphosphonium bromide (Chem. Abstracts Reg. No. 82667-45-6); and tris(hydroxymethyl)(1-hydroxy-2-propenyl)phosphonium salts (Chem. Abstracts Reg. No. 73082-48-1).

- An example of a polymerizable monomer that contains both a weak acid group and a strong cationic group is N-(4-carboxy)benzyl-N,N-dimethyl-2-[(2-methyl-1-oxo-2-propenyl)-oxy] ethanaminium chloride ($\text{HOOC-C}_6\text{H}_4\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OCC}(\text{CH}_3)=\text{CH}_2$), which can be prepared by reacting 2-(dimethylamino) ethyl acrylate with 4-(chloromethyl) benzoic acid.

- It is possible to add strong cationic functionality to an already prepared polymer. For example, a polymerizable monomer having a weak acid group can be copolymerized with a vinylbenzyl halide to form a polymer having a weak acid group and a benzyl halide group. This polymer can then be post-reacted with a nucleophile such as a tertiary amine or a dialkyl sulfide, which can displace the halide group and form a benzyonium salt:



- where A is a pendant weak acid group; Ar is an aromatic group, preferably a phenyl group; L is a leaving group, preferably a halide group, more preferably a chloride group; and Nu is a dialkyl sulfide such as dimethyl sulfide and diethyl sulfide; a cyclic sulfide such as tetrahydrothiophene; or a tertiary amine such as trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, and triethanol amine. The leaving group, L, can be replaced with a bicarbonate counterion by any suitable method, such as those described herein.

Examples of non-interfering polymerizable monomers include acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, glycidyl acrylate, and allyl acrylate; methacrylates such as

methacrylate, ethyl methacrylate, butyl methacrylate, allyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate; alkenyl aromatic hydrocarbons such as 4-methacryloxy-2-hydroxy-benzophenone, 2-(2'-hydroxy-5-methacryloxyethylphenyl)-2H-benzotriazole; and

5 C₁-C₄ alkyl- or alkenyl-substituted styrenes, preferably styrene, α -methylstyrene, vinyltoluene, and divinylbenzene. Other examples of non-interfering species include C₃-C₁₈-perfluoroalkyl methacrylates such as 2-(perfluorooctyl)ethyl methacrylate; C₃-C₁₈-perfluoroalkyl acrylates such as

2-[ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl 2-propenoate; and C₃-C₁₈-

10 perfluoroalkyl vinylbenzenes. (See U.S. Patent 4,929,666, column 4, lines 54 to 68, and column 5, lines 1 to 30.)

The presence of UV absorbing species such as 4-methacryloxy-2-hydroxy-benzophenone and 2-(2'-hydroxy-5-methacryloxyethylphenyl)-2H-benzotriazole into the polymer backbone can provide a protective barrier for human skin against the

15 sun.

A composition which comprises an aqueous-based solvent and a water-compatible polymer having a bicarbonate counterion can be prepared from the polymer with the non-bicarbonate counterion. The term "aqueous-based solvent" is used herein to refer to a solvent that contains water, and optionally a water-miscible

20 organic solvent. Examples of suitable water-miscible solvents include alcohols, preferably C₁-C₄ alcohols, more preferably ethanol and isopropanol; ethers such as tetrahydrofuran and 1,4-dioxane; glycols such as ethylene glycol and propylene glycol; C₁-C₄ alkylene glycol monoalkyl or dialkyl ethers such as the monomethyl, monoethyl, monobutyl, dimethyl, diethyl, dibutyl, and ethylmethyl ethers of ethylene

25 glycol and propylene glycol; C₁-C₄ dialkylene glycol dialkyl ethers, such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, and diethylene glycol dibutyl ether; acetone; dimethylformamide; and N-methylpyrrolidone. Carbon dioxide can also be used as a cosolvent.

The solution comprising an aqueous-based solvent and the water-compatible

30 polymer having a bicarbonate counterion can be prepared by the steps of:

1) precipitating the polymer having a non-bicarbonate counterion by adding dilute base to a first solution comprising a first aqueous-based solvent and the polymer;

2) isolating and washing the precipitate with water; and 3) redissolving the polymer in a second aqueous-based solvent and carbon dioxide and/or carbonic acid.

This preparation replaces at least a portion of the non-bicarbonate ions with bicarbonate ions and removes at least a portion of the non-bicarbonate ions from the solution. The replacement of the non-bicarbonate ion with the bicarbonate ion is sufficient to render the polymer soluble in the second aqueous-based solvent. Preferably, not less than 20 percent, more preferably not less than 50 percent, even more preferably not less than 70 percent, and most preferably not less than 90 percent of the non-bicarbonate ions are replaced with bicarbonate ions.

The pH of the composition comprising the redissolved polymer and the second aqueous-based solvent is sufficiently low to render and keep the polymer soluble in the solvent. The pH is preferably not higher than the pK_a of the weak acid group, more preferably not higher than 5, and most preferably not higher than 4. The first and second aqueous-based solvents may be the same or different.

The polymer requires a sufficient concentration of weak acid groups, anions of weak acid groups, and strong cationic groups (the sum of which is referred to hereinafter as the "total potential charge") to render the polymer soluble in the aqueous-based solvents. Preferably, the total potential charge is not less than 0.05, more preferably, not less than 0.1, and most preferably, not less than 0.5 meq of total potential charge per gram of the polymer. Preferably, the total potential charge is not more than 10, more preferably not more than 6, and most preferably not more than 3 meq of total potential charge per gram of the polymer.

Preferably, the non-interfering polymerizable monomer comprises not less than about 50 mole percent, more preferably not less than about 70 mole percent, and most preferably not less than about 90 mole percent of the total monomers used to prepare the soluble polymer.

A preferred method of preparing a stable aqueous colloidal dispersion (that is, a latex) comprising a continuous phase and a dispersible polymer having a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion comprises the steps of: 1) preparing a seed latex; 2) diluting the seed latex with water; 3) contacting the diluted solution

with a radical initiator, a polymerizable ethylenically unsaturated monomer or monomers having at least one weak acid group and at least one strong cationic group associated with a non-bicarbonate counterion; 4) polymerizing the solution from step 3 under such conditions to form a latex having pendant strong cationic groups and pendant weak acid groups; and 5) exchanging the non-bicarbonate counterion with bicarbonate and removing the non-bicarbonate counterion.

The seed latex is preferably prepared by emulsion polymerization in a batch process using a cationic or non-ionic surfactant, more preferably a cationic surfactant. The seed latex acts as a locus of polymerization for subsequent monomer addition, so that the formation of new particles is minimized and greater uniformity in the distribution of particle size in the final product is achieved. Thus, the monomer or monomers used to prepare the seed latex are chosen to form particles that have an affinity for the monomers subsequently added, so that polymerization occurs preferentially in or on the seed latex particles. The extent to which the seed latex is diluted in step 2 is a function of the desired particle size and the percent solids in the final latex, and can be readily determined by one of ordinary skill in the art.

Preferably, the amount of the non-interfering polymerizable monomer used to prepare the latex generally composes up to 98 mole percent of the monomers used to prepare the polymer. Preferably, the non-interfering polymerizable monomer comprises not less than about 50 mole percent, more preferably not less than about 75 mole percent, and most preferably not less than about 90 mole percent of the total monomers used to prepare the latex. The total potential charge of the latex is preferably not more than 3, more preferably not more than 2, and most preferably not more than 1 meq/g of polymer. The total potential charge of the latex is preferably not less than 0.05, more preferably not less than 0.1, and most preferably not less than 0.2 meq/g of polymer.

The non-bicarbonate ion can be exchanged with a bicarbonate ion in step 5, preferably by first saturating under pressure an aqueous-based solution or dispersion of the polymer with carbon dioxide, either as dry ice or as a gas, then contacting the CO₂-saturated polymer dispersion with an ion-exchange resin that contains bicarbonate functionality such as DOWEX™ Monosphere 550A anion-exchange resin (a trademark of The Dow Chemical Company) in the bicarbonate form. The pH of the

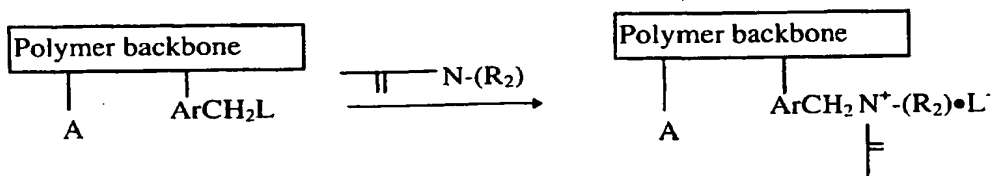
composition comprising the stable aqueous dispersion of the polymer is sufficiently low to render the polymer stable in the continuous phase, preferably lower than the pK_a of the weak acid group, more preferably not greater than 5, and most preferably not greater than 4.

- 5 It is also possible to prepare a stable aqueous dispersion from a preformed polymer having at least one pendant weak acid group and at least one pendant strong cationic group associated with a non-bicarbonate counterion. The preformed polymer can be dissolved in a suitable solvent, then dispersed in water by any suitable method. The solvent can then be removed and the solids content adjusted
10 to form a so-called artificial latex. This non-bicarbonate counterion can then be exchanged with a bicarbonate counterion.

- When a composition containing an aqueous-based solvent and the dissolved polymer is applied to a substrate, the weak acid becomes deprotonated upon evolution of carbon dioxide. The now deprotonated acid is available to form an ion
15 pair with a strong cation of the same or different polymer backbone, thereby producing a material that is incompatible with the aqueous-based solvent. Inasmuch as the anion is the conjugate base of a weak acid, a weak acid such as an aqueous solution of vinegar or citric acid is sufficient to break up ionic pairing, thereby allowing for the easy removal of the coating from the substrate.

- 20 The water-incompatible coating can be subsequently heated or irradiated with UV light to form a permanent coating, that is, a coating that is resistant to removal by aqueous-based acids or bases, provided the polymer contains crosslinkable groups such as benzyonium groups, glycidyl groups, or allylic groups. A coating that contains these UV-crosslinkable groups is particularly useful as a photoresist for
25 printed circuit boards.

 It is further possible to form a permanent coating by post-reacting crosslinking functionality onto the polymer backbone, as illustrated.



For example, vinylbenzyl chloride can be copolymerized with acrylic acid to
 5 form a polymer containing acid and benzyl chloride functionality. The polymer can
 then be post-reacted with an ethylenically unsaturated tertiary amine such as
 dimethylaminoethyl-methacrylate to form a compatible, crosslinkable quaternary
 ammonium chloride, which can then be exchanged with bicarbonate. This solvent-
 compatible, crosslinkable polymer can then be applied to a surface to subsequently
 10 form a coating and crosslinked by any suitable method such as radical initiated
 polymerization.

In another preferred aspect of the present invention, a permanent coating can
 also be prepared from a latex. Application of the latex to a substrate causes loss of
 CO₂ and a dry-to-the-touch film. The dry latex-based film is resistant to acidic or
 15 basic water-based solvents.

The compositions of the present invention may also contain dyes, fillers,
 pigments, anti-bacterial agents, fungicides, anti-oxidants, and perfumes. These
 compositions are useful as floor coatings; wood primers; skin care products including
 moisture barriers, sunscreens, and cosmetics; fingernail polishes; photoresists for
 20 printed circuit boards; paints, particularly latex spray paints; automotive and aircraft
 coatings; liquid- and gas-permeable membranes; coatings for fabrics; and hair care
 products.

The following examples are for illustrative purposes only and are not intended
 to limit the scope of this invention. All percentages are based on weight unless
 25 otherwise indicated.

Example 1 - Preparation of a Removable Coating from a Dissolved Polymer

Four liquid streams were added simultaneously and continuously to a
 nitrogen-purged reaction vessel maintained at 60°C and containing water (30 g) and

2-propanol (30 g). The liquids were added over five hours. The liquid streams were identified as follows.

Stream	Component	Amount
1	methyl methacrylate	78.1 g (0.78 mole)
	acrylic acid	7.95 g (0.11 mole)
2	water	75 g
	M-quat ^a	30.9 g ^b (0.11 mole)
3	2-propanol	75 g
	2,2'- azobis(2,4-dimethylpentane nitrile) ^b	1.00 g
4	water	45 g
	2-propanol	45 g

^a 2-(methacryloyloxy)ethyl] trimethylammonium chloride obtained as a 74 percent aqueous solution from Bimax Inc., 717 Chesapeake Ave., Baltimore, MD 21225

5 ^b obtained from E. I. du Pont de Nemours and Co.

After the addition was complete, the reaction solution temperature was maintained at 60°C for an additional 2 hours. The solution was then cooled, whereupon a portion of the solution (29.3 g) was added with stirring to a sodium carbonate solution (275 mL, 0.2 M). After stirring for 10 hours, the product, which
 10 was a stringy gel, was isolated by filtration, followed by immersion in water (500 mL) for 1 hour. Filtration and immersion were repeated four times before the isolated gel was dried under vacuum to yield 11.7 g of solid polymer.

A solution containing 5 percent of the dried polymer, 5 percent of N-methyl pyrrolidone, 45 percent 2-propanol, and 45 percent water was prepared. Dry ice was
 15 added to facilitate dissolution of the polymer. A portion of the formulation was applied to a painted metal surface, then drawn along the surface with a KIMWIPES™ EXL tissue (a trademark of Kimberly Clark Corporation, Roswell, GA 30076-2199) to produce a thin coating. After 1 minute, the resulting clear coating was dry to the touch and resistant to running water. After 4 hours the hard coating could not be
 20 removed by rubbing 30 times with a cotton swab wetted with either water or isopropanol. The coating was removed with a solution of 0.1 N citric acid dissolved in a 1:1 mixture of water and isopropanol.

Example 2 - Preparation of a Composition for Mammalian Skin Applications

The liquid streams were identified as follows:

Stream	Component	Amount
1	methyl methacrylate	32.2 g (0.32 mole)
	acrylic acid	5.0 g (0.07 mole)
	2-hydroxyethylmethacrylate	48.4 g (0.37 mol)
	M-quat	14.4 g (0.05 mole)
2	sodium formaldehyde sulfoxylate	0.15 g ^c
3	t-butylhydroperoxide	0.29 g ^d

^cadded as a solution in 24 g of water

^d70 percent active, added as a solution in 24 g water

- 5 To a flask containing water (420 mL) and isopropanol (100 g) was added with stirring 9-mL shots of Stream 1, 2-mL shots of Stream 2, and 2-mL shots of Stream 3. The shots were added at 5-minute intervals until additions were completed. The reaction mixture was stirred at 50°C for three hours, whereupon the polymer was cooled down. An excess of dry ice and DOWEX™ Monosphere 550A
- 10 anion-exchange resin in the bicarbonate form was added to the solution with stirring for 5 minutes. The resin was then filtered off and the filtrate was collected and evaluated as a moisture barrier in the following manner.

- A portion of the filtrate was applied to the skin of a 3 to 4-week-old hairless mouse. The mouse was maintained on a diet deficient in essential fatty acids, which
- 15 caused high rates of water loss from the skin and severe scaling of the top layer of the skin. Daily topical applications of the formulation over a 5-day period resulted in reductions in trans-epidermal water loss (TEWL, as measured by a Servomed Evaporimeter) from 18 g/m²/hour to 10 to 12 g/m²/hour. A smoothing of the skin (that is, a reduction of scaling) was also observed.

20 **Example 3 - Preparation of a Coating from a Latex**

A latex was prepared using a 2-step process. First, a cationic surfactant stabilized polystyrene seed latex was prepared using a batch process. Second, a portion of the seed latex was used in a continuous addition process to prepare a film-

forming latex containing a carboxylic acid and a quaternary ammonium functional monomer.

A cationic polystyrene seed latex was prepared using octadecyltrimethylammonium chloride quaternary surfactant (20 g per 100 g of the styrene monomer).

- 5 A hydrogen peroxide/iron oxidation-reduction pair was used to initiate the styrene polymerization. The polymerization was carried out for 2 hours at 70°C under a nitrogen atmosphere. The resulting seed latex was 36.4 weight percent solids and its mean volume particle size (determined by hydrodynamic chromatography) was 343 Å.

- 10 Water (452 g) and a portion of the seed latex (8.8 g) were mixed together and transferred to a flask. The mixture was stirred at 60°C under a nitrogen purge for 30 minutes, whereupon the following liquid streams were continuously added over 4 hours:

Stream	Component	Amount
1	methyl methacrylate	124 g (1.24 mole)
	butyl acrylate	176 g (1.38 mole)
	methacrylic acid	5.3 g (0.06 mole)
2	water	16 g
	M-quat	17.3 g* (0.06 mole)
3	water	16 g
	t-butylhydroperoxide	1.82 g
4	water	16 g
	sodium formaldehyde sulfoxylate	0.96 g

- 15 After the addition was completed, the mixture was stirred for an additional 1 hour, then allowed to cool. The resulting dispersion was milky white. Hydrodynamic chromatography showed a mean volume particle size of 1785 Å. The following ion-exchange process was used to convert the cationic latex. DOWEX™ Monosphere 550A anion-exchange resin in the bicarbonate form, (10 mL) was added
- 20 to a first vessel. The first vessel was flushed with 3 volumes of CO₂ gas then pressurized to 30 psig with CO₂ gas. A portion of the prepared latex was placed in a

second vessel, which was flushed twice with CO₂ gas, then pressurized to 30 psig with CO₂ gas. The second vessel was placed in an ice water bath and shaken intermittently for 10 minutes to maximize CO₂ absorption into the latex. The contents of the second vessel were transferred to the first vessel under a positive pressure of CO₂ gas. The latex remained in contact with the anion-exchange resin under a positive pressure of CO₂ gas until ready for use.

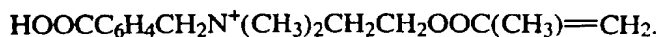
A film of the latex was cast onto a glass plate using a 10-mil draw down cup under ambient conditions (22.4°C, 65 percent relative humidity). In less than 1 minute of air exposure, a film formed that was dry to the touch.

10 Example 4

A polymer gel was prepared, precipitated, and washed (but not dried) as described in Example 1. The isolated gel (28.6 g, 9.30 weight percent solids), the monomethyl ether of propylene glycol (3.2 g), propylene glycol (0.80 g), and 2-propanol (0.70 g) were all loaded into a pressure vessel. The vessel was pressurized under CO₂ to 275 kPa (40 lb/in²) and shaken for 1 hour, to dissolve the gel. A coating was prepared by first allowing a portion of the solution to escape through a valve onto a painted substrate, followed by drawing down a film with a KIMWIPES™ EXL tissue. After 1 minute, the film was dry to the touch, and after 10 minutes, the coating could not be removed by 20 wipings with a water-wet cotton swab. The coating was removed with a solution of 0.1 N citric acid dissolved in a 1:1 mixture of water and isopropanol.

CLAIMS:

1. A polymer comprises a backbone with at least one pendant weak acid group and at least one pendant strong cationic group associated with a bicarbonate counterion, wherein the strong cationic group is formed from the polymerization of a trialkylammoniumalkyl acrylate, a trialkylammoniumalkyl methacrylate, a trialkylammoniumalkyl acrylamide, a 2-methacryloxyethyl-tri-C₁-C₂₀-alkyl-phosphonium salt, a C₃-C₁₈-alkenyltrialkyl-phosphonium salt, or by the polymerization of a monomer that contains both strong cationic groups and weak anionic groups.
2. The polymer of Claim 1 which is dissolved in an aqueous-based solvent.
3. The polymer of either Claim 1 or 2 which includes units formed from the polymerization of methyl acrylate, ethyl acrylate, butyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, allyl acrylate, glycidyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, allyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, a C₃-C₁₈-perfluoroalkyl methacrylate, a C₃-C₁₈-perfluoroalkyl acrylate, a C₃-C₁₈-perfluoroalkyl vinylbenzene, styrene, α -methylstyrene, or vinyltoluene.
4. The polymer of any of Claims 1 to 3 wherein the pendant weak acid is formed from the polymerization of acrylic acid, methacrylic acid, itaconic acid, β -carboxyethyl acrylate, vinylbenzoic acid, vinylchlorophenol, vinylbromophenol, vinylthiophenol, or 2-propenoic acid: 2-methyl-, (hydroxyphosphinyl) methyl ester.
5. The polymer of any of Claims 1 to 4 wherein the pendant strong cationic group is formed from the polymerization of 2-[(methacryloyloxy)ethyl] trimethylammonium chloride, and the pendant weak acid group is formed from the polymerization of acrylic acid or methacrylic acid.
6. The polymer of any of Claims 1 to 3 wherein the pendant strong cationic group is formed from the polymerization of:



7. A composition comprising a stable aqueous dispersion of a polymer having a backbone containing pendant weak acid groups, and pendant strong cationic groups associated with bicarbonate counterions wherein the composition has a pH of not greater than 5.

- 5 8. The composition of Claim 7 which is prepared by the steps of:
- a) continuously adding to a mixture of water and a cationic surfactant stabilized polystyrene seed latex a polymerizable monomer containing a weak acid group, a polymerizable monomer containing a strong cationic group associated with a non-bicarbonate counterion, and a non-interfering polymerizable monomer;
- 10 b) polymerizing the polymerizable monomers under such conditions to form a stable aqueous dispersion having pendant strong cationic groups associated with non-bicarbonate counterions, pendant weak acid groups, and pendant non-interfering groups; and c) saturating the dispersion with CO₂ under pressure, then contacting the CO₂-saturated dispersion with an ion-exchange resin that contains bicarbonate
- 15 functionality, thereby exchanging the non-bicarbonate counterion with bicarbonate.

9. The composition of Claim 8 wherein the non-interfering polymerizable monomer is methyl acrylate, ethyl acrylate, butyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, allyl acrylate, glycidyl acrylate, methyl methacrylate, ethyl methylacrylate, butyl methacrylate, allyl methacrylate, glycidyl methacrylate,
- 20 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, a C₃-C₁₈-perfluoroalkyl methacrylate, a C₃-C₁₈-perfluoroalkyl acrylate, a C₃-C₁₈-perfluoroalkyl vinylbenzene, styrene, α-methylstyrene, or vinyltoluene.

10. The composition of either Claim 8 or 9 wherein the non-interfering polymerizable monomer is methyl methacrylate, butyl acrylate, 2-hydroxyethyl
- 25 methacrylate, 4-methacryloxy-2-hydroxy-benzophenone, or 2-(2'-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole and the amount of the non-interfering polymerizable monomer used to prepare the stable aqueous dispersion represents from 90 to 98 percent of the monomers used to prepare the polymer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/00726

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F220/04 C08F220/34 C08F8/00 C08F212/14 C08F220/60
C08F230/02 C09D157/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 183 158 A (THE DOW CHEMICAL CO.) 4 June 1986	
A	EP 0 000 426 A (THE UNIVERSITY OF MELBOURNE) 24 January 1979	
A	EP 0 239 035 A (BASF A.G.) 30 September 1987	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "&" document member of the same patent family

Date of the actual completion of the international search

5 June 1997

Date of mailing of the international search report

11.06.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Cauwenberg, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/00726

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 183158 A	04-06-86	AU 593225 B AU 4897885 A CA 1262798 A JP 61130306 A	08-02-90 28-05-87 07-11-89 18-06-86
EP 426 A	24-01-79	AU 3747378 A	21-02-80
EP 239035 A	30-09-87	DE 3609829 A CA 1329678 A JP 62232413 A US 4748220 A	24-09-87 17-05-94 12-10-87 31-05-88